



	<b>Experiment title:</b> High energy powder diffraction on metal decorated graphenes	<b>Experiment number:</b> CH- 656
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<b>Shifts:</b> 12	<b>Local contact(s):</b> Dr Michela BRUNELLI, Dr Simon KIMBER	<i>Received at ESRF:</i>
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## Report:

Graphene displays very promising features in the field of energy storage. In particular, the possibility of developing graphene-based solid state hydrogen storage systems is attractive in order to meet the stringent requirements imposed by US-DOE for the automotive industry [1].

Chemically produced graphene compounds appear particularly suitable for developing efficient gas storage systems, in virtue of its high porosity (up to 2630 m<sup>2</sup>/g specific surface) and lightweight. But hydrogen molecule interacts too weakly with the bare sp<sup>2</sup> carbon plane to be useful as it is (H<sub>2</sub> binding energy of 5kJ/mol) [1]. Nevertheless, recent theoretical works indicated that it is possible to bring this value in the range 20-40 kJ/mol, which represents the ideal binding energy for a reversible storage system, by “decorating” graphene layers with metal ions, in particular alkali, alkali earth and transition metal ions [2].

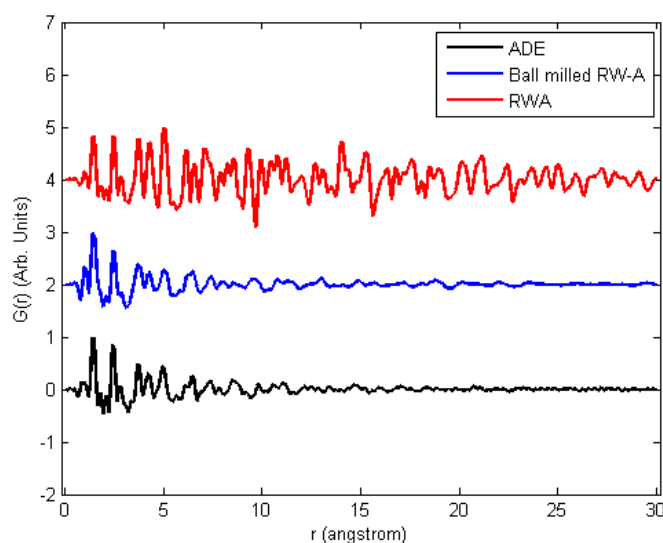
We managed to produce gram-scale graphene samples following an efficient chemical method, based on the thermal exfoliation of graphite oxide in inert atmosphere [3]. In this system, the graphene sheets are highly defective, either for the presence of carbon vacancies in the sp<sup>2</sup> carbon network or for the presence of unsaturated edges. These defects could be very reactive and have high capture cross section for other chemical species, thus working as anchors for further functionalization [4].

Thanks to these, we also successfully prepared metal decorated graphene, by using chemically produced highly defective graphene as precursor. In particular, we synthesized graphene samples decorated with lithium and nickel, which indeed appeared very promising as hydrogen absorbers [5].

Nevertheless, a clear knowledge of the defective graphene samples morphology and of the defects at atomic level, as well as of the position of the decorating metal ions, with respect the carbon layer, is still missing: this is mainly due to the fact that samples lack of crystalline order, this being retained only at the nanoscale.

For this reason, we performed high-energy X-ray diffraction and atomic pair distribution function (PDF) data analysis on either as-prepared graphene, or metal (Li, Ni) decorated graphene on the beamline ID15B. We used monochromatic x-ray beam with  $\lambda = 0.22235 \text{ \AA}$  collimated on the the samples sealed in 0.5 glass capillaries in Ar atmosphere, in order to avoid oxygen and moisture contamination. Diffraction data for PDF were acquired with an image plate detector, MAR345, placed at 20 cm distance from the sample. This configuration allowed us to collect data at  $Q$  up to  $22 \text{ \AA}^{-1}$ . Typical acquisition time for each scan was 10 seconds; in order to improve the statistics, 10 scans were summed together for each measurement. In order to subtract spurious contributions, blank measurements were performed either on the empty capillary or on the air. “Standard” diffraction was also collected for each sample by placing the detector far away from the sample, at 60 cm distance. The temperature of the samples was varied in the range 90 K – 300 K, thanks to the use of a nitrogen cryocooler, placed very closed to the sample.

Data reduction was performed with freeware software. In particular, we used Fit2D to extract diffraction pattern from the 2D images. We then used PDFGetX3 to extract the  $G(r)$  function from the data and then the PDFGui suite to fit the experimental data with the calculated PDF from our models. Data analysis is still in progress, however preliminary data clearly show differences between PDF of graphene, pure graphite and ball milled graphite (see Figure 1). In the figure, one can see that the progressive reduction of the dimensionality of the system, obtained with mechanical action, in case of ball milled graphite, or by chemical processes, in case of chemical produced graphene, strongly affects the intensity of the peaks at large  $r$  of the PDF function. We are currently developing a model to describe the PDF profile in these two cases and to extend the analysis also on the decorated graphene samples.



**Figure 1:** Comparison of extracted PDF of pure graphite (RW-A SGL Carbon, in red), ball milled graphite (in blue) and chemically produced graphene (in black).

## References

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